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This is to announce that beginning in 1954 publication of the *Canadian Journal of Technology* will be on a bimonthly basis. The first number to be published according to the new schedule will be issued in January; subsequent issues will appear in alternate months.

The subscription rate effective 1 January 1954 will be $3.00.

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THE EFFECT OF κ- AND λ-CARRAGEENINS ON THE VISCOSITY OF MILK[1]

BY DAVID B. SMITH

ABSTRACT

The marked enhancement of milk viscosity by carrageenin is due to the κ-component, a fraction precipitated from dilute solutions of the whole polysaccharide by the addition of potassium salts. The potassium ion level of milk is necessary for the maximum viscosity-increasing effect.

Carrageenin, an extract from *Chondrus crispus*, and some related red algae, has recently been separated (2) into two distinct fractions. The fraction gelled or precipitated by added potassium salts has been termed κ-carrageenin; the fraction unaffected by potassium ions, λ-carrageenin. Carrageenin from *Chondrus crispus* contains these fractions in approximately equal amounts (2).

The principal commercial use of carrageenin is to stabilize the cocoa suspension in chocolate milk by a marked enhancement of the viscosity of milk (1). It was, therefore, of interest to compare the effects of the two fractions on milk viscosity. Because of the action of potassium ion on carrageenin, the effect of variations in the potassium concentration on the viscosity of carrageenin–milk mixtures was also investigated.

MATERIALS AND METHODS

Three samples of commercial carrageenin, designated as CM-1, C-3, and C-4, having intrinsic viscosities of 9.6, 11.2, and 4.1 respectively, were used in this investigation. The κ-carrageenin fraction was precipitated from each by adding, with rapid stirring, 1.0 *M* potassium chloride to 0.1% carrageenin solutions in water until the potassium chloride concentration was 0.15 *M*. After centrifuging in a high speed angle centrifuge, the supernatants, containing the λ-carrageenin, were easily decanted. The κ-carrageenin precipitates were dissolved in 0.1 *M* sodium chloride and reprecipitated with three volumes of ethanol. The λ-carrageenin fractions were recovered from the supernatants by the addition of three volumes of ethanol. The fractions were separated from the alcohol by decantation and centrifugation, washed with 80% ethanol

[1] *Manuscript received July 27, 1953.*
Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 288 of the Canadian Committee on Food Preservation and as N.R.C. No. 3082.

to remove salts, and dried with absolute alcohol and ether. Retreatment of κ-CM-1 and λ-CM-1 each by the same procedure separated a small amount of contaminating λ-carrageenin from κ-CM-1 but precipitated no material from λ-CM-1. 0.75% solutions of the three carrageenin samples and their fractions were dialyzed exhaustively against 0.08 *M* sodium chloride to ensure complete conversion to the sodium salts. After clarification by centrifugation, the concentrations were determined refractometrically and adjusted to 0.6% with 0.08 *M* sodium chloride.

Three different samples of homogenized pasteurized milk were used. Increases in the salt content of one sample of milk were made by dissolving salts in the milk. The potassium content of another sample of milk was reduced by dialysis against two changes of a potassium-free buffer over 24 hr. at 3° C. Another portion of the same milk was dialyzed similarly against a potassium-containing buffer. The latter buffer was prepared to simulate the electrolyte content of milk by dissolving, per liter of buffer, 0.51 gm. calcium hydroxide, 2.35 gm. citric acid, 0.98 gm. Na_2HPO_4, 2.39 gm. potassium chloride, 0.17 gm. potassium sulphate in 700 ml. water, adding 1.0 *M* sodium hydroxide to a pH of 6.8 and water to one liter. The potassium-free buffer differed from the above only in the replacement of the potassium salts with equivalent amounts of the corresponding sodium salts. The ionic strengths of these buffers were about 0.08.

Mixtures of milk and carrageenin were prepared by weighing 2.5 gm. of 0.6% carrageenin solution into 50 ml. volumetric flasks and filling to volume with milk. After warming the flasks to 60° C. in a water bath, the contents were poured into bottles, which were stoppered and stored overnight at 3° C. The concentration of carrageenin in these mixtures was 0.03%. Blank mixtures, containing no carrageenin, were made up with 2.5 gm. 0.08 *M* sodium chloride.

Viscosity measurements were made at 10° C. in an ASTM No. 100 Fenske-Ostwald viscometer. Flow times were recorded only for the first passages through the capillary (1). Duplicate determinations were made with new fillings of the instrument.

RESULTS AND DISCUSSION

Viscosities of mixtures of milk and carrageenin, relative to the viscosities of the corresponding blank mixtures, are given in Table I. Because of considerable variation between milk samples in their response to carrageenin (1), only results involving a single milk sample should be compared.

Milk viscosity was increased much more by κ-carrageenin than by the λ-fraction. The effect of unfractionated carrageenin lay between those of the two fractions. The κ-fraction of a carrageenin sample of high intrinsic viscosity, C-3, caused a greater increase in viscosity than that obtained from a low viscosity sample, C-4.

The effect of potassium ions is shown by the results with milk sample No. 2. The lower results of the milk dialyzed against the potassium-containing buffer compared with those obtained with untreated milk were due to dilution of the milk during dialysis. The viscosity, relative to water, of the blank mixture

TABLE I

VISCOSITIES OF MILK–CARRAGEENIN MIXTURES

Material	Milk sample No.	Treatment of milk	Viscosity*
C-3	1	None	5.83
κ-C-3	1	None	8.55
λ-C-3	1	None	1.91
C-4	1	None	3.60
κ-C-4	1	None	6.13
λ-C-4	1	None	1.52
CM-1	2	None	4.69
κ-CM-1	2	None	8.95
λ-CM-1	2	None	2.73
CM-1	2	Dialyzed vs. K-free buffer	1.49
κ-CM-1	2	Dialyzed vs. K-free buffer	2.05
λ-CM-1	2	Dialyzed vs. K-free buffer	1.51
CM-1	2	Dialyzed vs. K-cont. buffer	1.76
κ-CM-1	2	Dialyzed vs. K-cont. buffer	5.62
λ-CM-1	2	Dialyzed vs. K-cont. buffer	1.52
C-4	3	None	4.28
C-4	3	0.04 *M* KCl added	4.80
C-4	3	0.04 *M* NaCl added	4.37

* *Viscosity relative to carrageenin-free milk blank.*

of untreated milk was 1.95 and of the potassium-containing dialyzed milk, 1.72. The milk dialyzed against the potassium-free buffer was diluted similarly, and its blank mixture had a relative viscosity of 1.69. In spite of this dilution, however, the results show that the effects of the κ-fraction and unfractionated carrageenin were much lower in potassium-depleted milk than in milk dialyzed against the potassium-containing buffer. The effect of λ-carrageenin was unaltered by reducing the potassium content of the milk.

Since doubling the potassium ion content of milk sample No. 3 resulted in only a small increase in viscosity (Table I), the natural potassium content of milk (about 0.04 *N*) must be nearly sufficient to bring out the full effect of added carrageenin.

For comparison with the viscosities of milk–carrageenin mixtures (Table I), the following viscosities, relative to the water, of 0.03% solutions of CM-1 and its fractions in salt solutions are given:

Material	In 0.04 *M* KCl + 0.04 *M* NaCl	In 0.08 *M* NaCl
CM-1	1.42	1.28
κ-CM-1	1.87	1.21
λ-CM-1	1.45	1.45

These results show that the interaction of potassium and carrageenin at effective stabilizing concentrations is alone insufficient to account for the viscosity increase observed in milk (Table I).

Previous work (1) indicated that the viscosity of milk was increased by the interaction of the carrageenin with a milk constituent, probably casein. The present work shows that the potassium sensitive fraction, κ-carrageenin, is mainly responsible for this effect. It is also shown that potassium ions must be present in about the proportions found in milk to obtain maximum increase in viscosity. The viscosity increasing or stabilizing power of carrageenin in milk depends therefore on an interaction between potassium ions, a milk constituent, and the κ-fraction of carrageenin.

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METHODS OF ANALYSIS FOR SOLANINE IN TUBERS OF *SOLANUM TUBEROSUM*[1]

By D. H. Dabbs[2] and R. J. Hilton[3]

ABSTRACT

Investigational work was carried out in an effort to obtain a shorter method of quantitatively estimating the solanine content of a sample of potato tubers. As a prerequisite to the investigation, a sample of pure solanine was isolated from potato sprouts and purified. An analytical procedure was evolved, by an amalgamation of two existing methods, which was used as a Standard Method in this study. Unsuccessful attempts were made to estimate the solanine content of potatoes by: using qualitative reagents on fresh tuber slices; a simplification of the regular extraction procedure; measuring the fluorescent intensity of solanidine; and extraction from dried tuber material.

A shortened analytical technique was eventually developed which enabled the investigator to complete duplicate analyses in about one-third the time required by the older methods. Fresh tuber material was extracted in a Soxhlet extraction apparatus, using acidified 95% ethyl alcohol as the solvent. The solanine content of this extract was estimated colorimetrically. Statistical analysis of duplicate solanine determinations gave a "*t*" value of only 0.03 for 30 degrees of freedom. The standard error of the method equals ±0.154 mgm. of solanine per 100 gm. of fresh tuber tissue, and these figures strongly indicate the reliability of the new, abbreviated analytical method.

INTRODUCTION

The problem of bitterness in table potatoes caused by the glycoalkaloid solanine is causing some concern in the Province of Alberta. This alkaloidal complex is apparently present in all potato tubers, but is normally present in very small amounts. In some seasons, at least a portion of the crop may have a very acrid flavor, and upon analysis will show a higher-than-average solanine content. Experimental work to date has resulted in many statements that are often contradictory regarding factors contributing to an excessively high content of this material in potato tubers.

Methods of solanine analysis, in use before this study was commenced, were long and involved. A shorter method of quantitative analysis was a necessary prerequisite to a comprehensive study of causal factors. The investigational work reported in this paper was carried out in an effort to obtain such a short analytical method.

Solanine is a glycoalkaloid which on acid hydrolysis yields one molecule each of glucose, galactose, and rhamnose, and a base, solanidine (6, 7, 13, 16). Workers have not reached complete agreement on the structural formula of solanine (2, 3, 15, 16). The properties of solanine have been determined by several workers (3, 4, 7, 13, 15, 16).

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Contribution from the Department of Plant Science, University of Alberta, Edmonton, Alberta. This paper is based on a thesis submitted by D. H. Dabbs in partial fulfillment of the requirements for the degree of Master of Science.

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The earliest work reported on solanine extraction from potato tubers was that of Morgenstern (10), published in 1907. In 1924, Bömer and Mattis (1) published results of their work on the 1922 and 1923 potato crop in Germany. Rooke and co-workers (13) criticized this early work and stated that these research analysts had applied methods of extraction of solanine from potato tissue which were subject to error and had used methods of determination which also were unsatisfactory. These workers had weighed the small amount of solanine obtained without particular knowledge of the purity of the substance. They also said that Bömer and Mattis (1) had applied too large a correction to their results. Rooke and co-workers (13) obtained a solubility figure of only 0.2 mgm. per 100 ml., as contrasted to 2.75 mgm. per 100 ml. given by the earlier workers.

The method of extraction developed by Pfankuch (11) was found by Rooke and co-workers (13) to be satisfactory, with some modifications. They also considered Pfankuch's colorimetric method of determination to be suitable and also the volumetric method advocated by Conner (3) appeared to provide an accurate estimation of solanine content.

Using Pfankuch's (11) colorimetric method of determination, Rooke and co-workers (13) proved that the unpurified solanine isolated in the normal course of determination in potatoes gave a color with maximum absorption at the same wave length as did pure solanine and pure solanidine, indicating that no interfering substance was present.

Wolf and Duggar (16) used a modified Bömer and Mattis (1) procedure for extracting solanine from tubers. They demonstrated that above a pH of 9.3 solanine was quantitatively insoluble in water. This was a most important contribution to the technique of solanine analysis, since by carrying out the precipitation of solanine at a controlled pH of 10.0 to 10.4, it became unnecessary to apply a solubility correction. These men noted that the use of a solubility correction factor by other workers gave variable and inaccurate results.

The most recent of the published methods of solanine analysis were studied in this laboratory. The best of these were found to be too long and cumbersome when a large number of tuber samples were to be analyzed within a limited period of time.

EXPERIMENTAL

(*a*) *Preparation of Pure Solanine*

A supply of pure solanine was essential in order that its properties could be studied and so that a calibration factor could be calculated for the particular colorimetric equipment being used. This could not be obtained from any North American or European source; hence it was necessary for the authors to isolate and purify their own sample. Only about six grams of the pure material were obtained from 85 lb. of finely ground potato sprouts.

The mashed sprout material was extracted with 2% acetic acid for 2–4 days, after which time a press was used to recover the extract. Concentrated ammonium hydroxide was used to precipitate the solanine. This precipitate was dried and then refluxed with 95% ethyl alcohol. The alcohol was filtered while

very hot, and upon cooling the solanine crystallized out in small, loose needles. This was filtered, refluxed, and crystallized from alcohol twice more.

The resulting crystals were then refluxed and filtered twice with diethyl ether to remove any traces of solanidine and solanthrene. The resulting solanine crystals were refluxed and crystallized twice more from 95% ethyl alcohol. By now the material crystallized out in snow-white, very small needles, and had a melting point of slightly over 283°C. The highest recorded melting point for pure solanine is 285°C. (15).

(*b*) *Standard Analytical Procedure*

The standard analytical procedure used was based upon a combination of the methods of Rooke *et al.* (13), and Wolf and Duggar (16).

The extraction procedure of Rooke was used, and the solanine was precipitated from the acidic extract by adjusting to pH of 10.0–10.4 with concentrated ammonium hydroxide, as suggested by Wolf and Duggar. The relatively large volume of solanine precipitate normally recovered in this investigation made it essential that this precipitate be dissolved from the filter paper with 75–80 ml. of 0.5% acetic acid. This extract was then diluted to 100 ml.

For the colorimetric determination of solanine plus solanidine (calculated as solanine), 3.0 ml. of the solanine solution was measured into a 50 ml. Erlenmeyer flask by means of a precision pipette. This was cooled in ice, and then, with vigorous shaking in the ice-bath, 6.0 ml. of concentrated sulphuric acid were added dropwise from a microburette. After one minute, 3.0 ml. of 1% formaldehyde were similarly added, drop by drop. The solanine content was determined after 45 min., using a Fisher Electrophotometer.

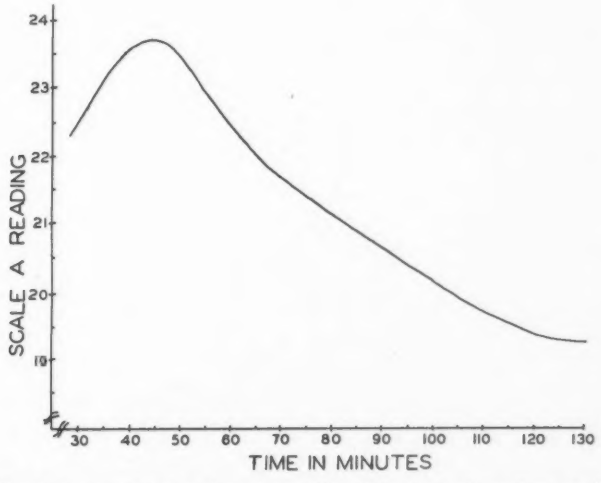

FIG. 1. Typical curve showing the relationship of the Scale A reading, of the violet-red color formed by solanine with sulphuric acid and formaldehyde solution, and the time in minutes after the addition of the last drop of formaldehyde.

A series of tests disclosed the fact that the maximum color intensity was reached between 40 and 50 min. after the last drop of formaldehyde had been added. This contrasts somewhat with the findings of Rooke and co-workers (13), who suggested a time-lapse of 90 min. for maximum color devlopment. Excellent results were obtained in this study by taking the highest reading during the 45–55 min. time-interval, using filter 525 (5250 Å).

A typical graph is shown in Fig. 1.

This standard analytical method gave reasonably good results, but a large number of individual steps were required which necessitated a long period of time for the completion of an analysis.

Table I illustrates typical solanine readings in duplicate as obtained with this modified Standard Method. The relationship between tubers noted as "bitter" from cooking tests, and a high solanine content, may be observed.

TABLE I

RESULTS OF SOLANINE ANALYSES USING MODIFIED STANDARD METHOD

Sample	Duplicate 1	Duplicate 2	Flavor after cooking
A	11.44	10.96	Not bitter
B	36.30	38.06	Bitter
C	11.04	10.73	Not bitter
D	9.51	9.51	Not bitter
E	37.50	35.80	Very bitter
F	78.32	80.37	Very bitter
G	32.91	31.43	Bitter

(*c*) *Results of Rapid Tests*

A number of methods designed to give a rapid estimation of the solanine content of tubers were tested and found to be unsatisfactory. The rose-violet color, obtained on immersing fresh tuber slices in a modified Bach reagent (8), would not consistently distinguish between tubers of high and low solanine content.

A fluorescence, such as that produced by solanine in solution when irradiated with ultraviolet light (16), could be detected under the skin of tuber slices after heating them for 30 min. at 90° in 4% hydrochloric acid, but it was impossible to estimate differences in the intensity of fluorescence. Extracts from the most bitter tubers analyzed failed to fluoresce strongly enough to excite the indicator of the Coleman fluorophotometer.

Attempts to materially shorten the regular extraction procedure by stirring or by using dried plant material were unsuccessful.

(*d*) *Improved Analytical Procedure*

An extraction technique was devised which used the Soxhlet type of extractor, with acidified 95% ethyl alcohol as the solvent. Solanine was extracted from finely pulverized, fresh tuber material. Early errors and disappointments

were experienced, but eventually what seemed to be a workable and very precise method of analysis was developed. The technique is described later in this section.

A series of duplicate extractions was arranged in an attempt to determine the minimum extraction period needed. Table II contains the results of these extractions, two colorimetric determinations having been made on each duplicate extract.

TABLE II

RESULTS OF A SERIES OF DUPLICATE SOLANINE EXTRACTIONS DESIGNED TO DETERMINE THE MINIMUM EXTRACTION PERIOD NECESSARY WITH THE SHORT SOXHLET METHOD

Mix No.	Extraction time (in hours)	Solanine content (mgm./100 gm. fresh tissue)
1	15	8.19
	17	8.19
	19	9.39
2	18	7.68
	20	7.76
	22	7.85
3	20	46.58
	22	46.58
	24	40.02

These figures indicate 20–22 hr. as the ideal extraction period. The loss of solanine in the 24-hr. extraction period may logically be due to a small amount of solanine breakdown because of an excessively long boiling period in the acidified alcohol.

Table III contains comparative solanine contents of several samples of potato tubers as determined concurrently on the same "mix" by means of the Short Soxhlet Method and the Long Standard Method.

These data indicate that the Soxhlet Method of extraction gave more consistent checks between duplicates, and usually indicated at least a slightly higher alkaloid content than did the old long method.

TABLE III

COMPARATIVE SOLANINE CONTENTS OF SEVERAL TUBER SAMPLES AS DETERMINED BY THE SHORT SOXHLET METHOD AND THE LONG STANDARD METHOD

Number of sample	Soxhlet*		Standard	
	Duplicate I	Duplicate II	Duplicate I	Duplicate II
A	35.07	34.13	32.91	31.43
B	37.20	36.52	34.75	34.35
C	66.18	65.44	68.34	67.83
D	7.34	7.68	3.50	4.05
E	46.88	46.28	44.79	41.98

**Samples B and C were extracted for 17 hr., while A, D, and E were extracted for 20 hr.*

Table IV contains the results of a series of duplicate Soxhlet extractions. Each figure is an average of two colorimetric determinations carried out on each extract.

The Soxhlet extraction technique used was as follows. The washed and dried tubers were sliced thinly and finely pulverized in a Waring Blendor. Duplicate 25.0 gm. samples were weighed in 50 ml. beakers and then transferred to 30 × 80 mm. Soxhlet thimbles. The beakers were thoroughly washed with 95% ethyl alcohol and these washings transferred to 250 ml. distilling flasks.

TABLE IV

DATA FROM A SERIES OF DUPLICATE SOXHLET EXTRACTIONS CARRIED OUT ON SEPARATE SAMPLES OF TUBERS (MGM. SOLANINE/100 GM. FRESH TUBERS)

Duplicate I	Duplicate II	Duplicate I	Duplicate II
37.20	36.52	8.45	7.93
16.55	17.75	7.34	7.68
46.88	46.28	7.93	7.76
66.18	65.44	7.68	7.85
46.88	46.28	7.68	7.68
50.28	49.54	25.68	26.02
17.66	18.17	35.07	34.13
8.11	8.22	40.31	39.72

A further 100 ml. of 95% ethyl alcohol was added to each flask, plus five drops of glacial acetic acid, and the Soxhlet apparatus assembled and placed on hot-plates to extract for 20–22 hr.

The extract was reduced in volume to 10–15 ml., *in vacuo*, in the distilling flask. Then 1.0 gm. of sodium sulphate was added to the distilling flask; it was swirled vigorously, and heated in a water-bath at 70°C. for 20–30 min., at which time a flocculent precipitate of protein material had formed. The extract was cooled, 0.5 ml. of 20% sulphuric acid was added, and the extract filtered through a 9 cm. Whatman's No. 4 paper; 10–15 ml. of 0.5% acetic acid was used to wash the distilling flask and the filter paper.

The filtrate was allowed to run into a 100 ml. beaker and the pH adjusted to 10.0–10.4 with concentrated ammonium hydroxide, using a Beckmann glass electrode pH meter. The precipitate was flocculated at 70°C. in a water-bath for 30 min. and was then cooled. The precipitate was either filtered off at this stage, or kept in a refrigerator overnight before being filtered. The solanine precipitate was filtered off through a 9 cm. Whatman's No. 42 paper, the precipitate being washed with about 10 ml. of 2% ammonium hydroxide. When no smell of ammonia remained on the filter paper, it was transferred to the same 100 ml. beaker used earlier, and the solanine was dissolved in several small increments of 0.5% acetic acid. The solanine solution was filtered through a qualitative filter paper into a 50 ml. volumetric flask. The paper was washed with 0.5% acetic acid, and the volume carefully made to the 50 ml. mark.

The solanine concentration was determined by reading the optical density of the violet-red color, produced by the sulphuric acid – formaldehyde reaction, in the same manner as was done with the Long Standard Method.

Wolf and Duggar (16) showed that a particularly close linear relationship existed between the concentration of solanine and the intensity of the color produced over the range of 5–10 mgm. per 100 ml. of solution. Accordingly, solanine solutions of higher concentration than this were diluted with 0.5% acetic acid until their concentrations fell within this range.

This analytical technique has made it possible to reduce the time factor to approximately one-third of that required by the old method. It was felt that any precision lost because of reducing the weight of fresh tissue to 25.0 gm. was more than compensated by the reduction in the numbers of individual steps and cumbersome transfers of large volumes of material.

DISCUSSION AND CONCLUSIONS

The negative nature of results for most of the trials reported herein bears out the complexity of solanine analytical procedure indicated by previous workers.

Solanine contents indicated by the Long Standard Method were not always reliable. It will be noted in Table III that in at least one instance the Soxhlet Method indicated approximately twice as much solanine as did the longer method. No reason could be found for this evident failure of the long method to extract more than about half of the alkaloid which was present.

When the solanine figures of Table IV were analyzed, a low and nonsignificant "t" value of 0.03 was obtained. The standard error (standard deviation of means) of the method was found to be $(S)/(\bar{n})$ equals ± 0.154 mgm. of solanine per 100 gm. of fresh tuber tissue. These figures strongly indicate the reliability of the shortened Soxhlet method of solanine estimation. This method represents what is felt to be a significant improvement in the procedure for the quantitative determination of this poisonous and troublesome glycoalkaloid.

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THE DETERMINATION OF THE HEAT OF AQUEOUS SOLUTION OF SOME HYPOPHOSPHITES AND CERTAIN OTHER MATERIALS[1]

By Norman F. H. Bright[2] and Thomas Carson

ABSTRACT

The heats of aqueous solution of the following materials have been determined over a range of concentrations using an adiabatic calorimeter:—sodium, ammonium, calcium, and barium hypophosphites (all anhydrous), barium hypophosphite monohydrate, ferrous oxalate dihydrate, hydrazine mononitrate, sodium permanganate mono- and tri-hydrates, and pentaerythritol. The accuracy in most cases is to within ±0.02 kcal./mole. In some cases, the data are suitable for calculating heats of dilution. The heats of solution at infinite dilution are quoted.

INTRODUCTION

The present research was undertaken to obtain heats of aqueous solution for certain materials required in connection with other work, for which data were not available in the current literature. The heats of solution were determined at various concentrations.

The materials included within the scope of the investigation were sodium, ammonium, calcium, and barium hypophosphites (all anhydrous), barium hypophosphite monohydrate, ferrous oxalate dihydrate, hydrazine nitrate, sodium permanganate mono- and tri-hydrates, and pentaerythritol. Mono-, di-, and tri-methylamine nitrates were also investigated but have been reported elsewhere (3).

EXPERIMENTAL

The calorimeter used in this work was an earlier model of an automatic adiabatic instrument described elsewhere (2). The instrument is shown in Fig. 1. The calorimetric technique did not differ in any significant way from that described therein; the degree of precision obtained, however, was not so high as in that work and will be discussed later.

Heats of solution were determined by measuring the thermal effects of successive small additions of the substance to a large volume of water, giving thereby a series of "differential heats" of solution at various concentrations. In the case of the more soluble materials, it was not practicable to make sufficient successive additions of solute to attain saturation, but with the less soluble materials it was found possible to provide a range of values for the "differential heat" of solution covering the whole range of solubility of the materials concerned. Again, no systematic investigation of the variation of these heats of solution with temperature was carried out, but throughout, an approximately constant temperature of 29°C. was used, this being found to be convenient for the satisfactory operation of the calorimeter.

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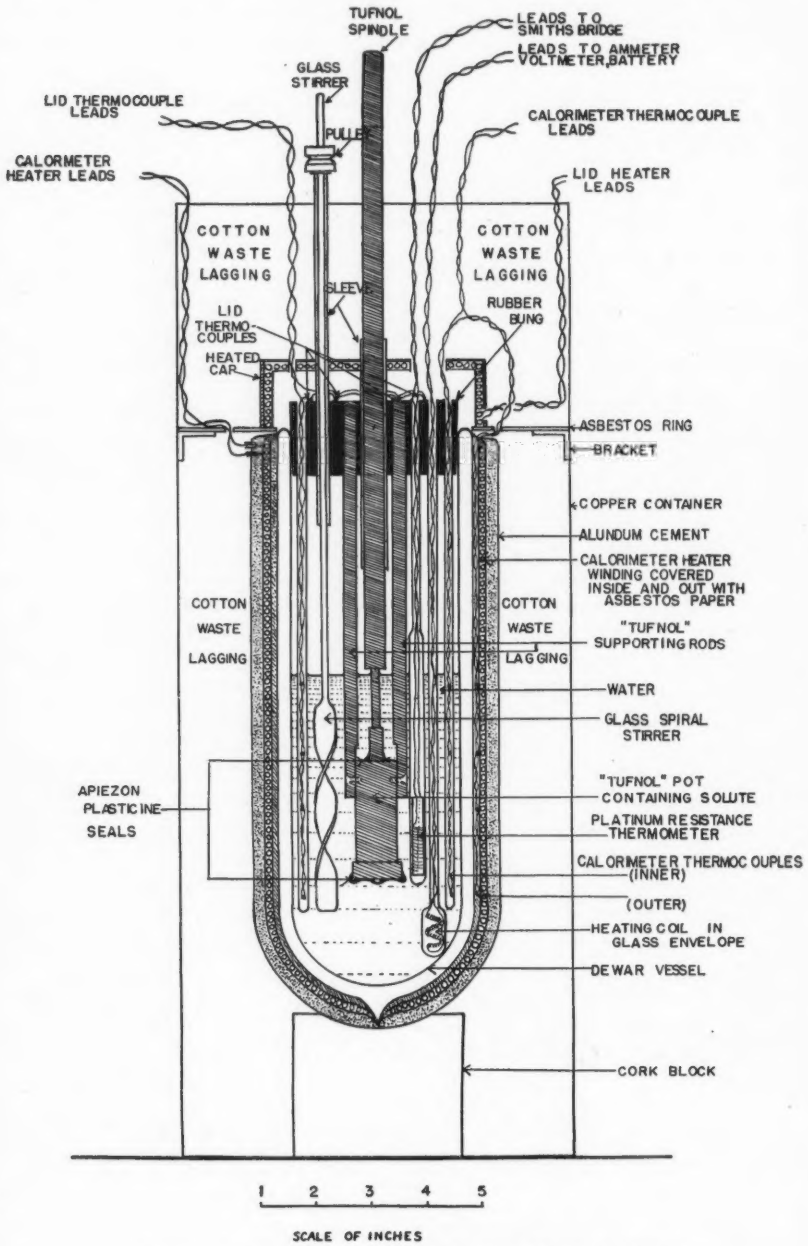

FIG. 1. Calorimeter used in determination of heats of solution.

The experimental technique involved the preparation of the materials in a dry state, either anhydrous if required, or as a definite hydrate free from excess water in the other cases, and in a fine state of division to accelerate their solution in the water.

(*a*) *Potassium Carbonate*

This was adopted as a standard material since its heat of solution has been well established. Berthelot and Ilosvay de Nagy Ilosva (1) quote the heat of solution of anhydrous potassium carbonate, $-\Delta H$, expressed in kcal./mole at a temperature t°C. as obeying the equation $-\Delta H = 6.50 + 0.074(t - 15)$. This is the heat of solution in 100 moles of water. Bichowsky and Rossini (*Thermochemistry of chemical substances*, Reinhold Publishing Company, 1936, pp. 157 and 392) quote the figure of 6.63 kcal./mole at 18°C. in 400 moles of water. The material used in the present investigation was of analytical reagent purity. It was prepared in the anhydrous state and inserted into a "Dry Box". Inside the dry box were dishes containing phosphorus pentoxide to maintain a desiccated atmosphere, and the necessary apparatus for filling the dry material into a "Tufnol"* vessel which was used as the container to go into the calorimeter. This vessel was equipped with a tightly fitting base and central rod by means of which the solute could be kept dry right up to the moment of release into the water. The pot was filled, closed, removed from the dry box, and reweighed as quickly as possible after closure, after which the gland at the top of the pot and the seal at the bottom were covered over with Apiezon vacuum plasticine to prevent ingress of water, either as vapor or as liquid. This technique ensured that the material was dried and sealed off in known quantity, without ever having been exposed either to atmospheric moisture or to contact with liquid water up to the moment of release into the water.

(*b*) *Calcium Hypophosphite*

The material available was of B.P.† quality. It is stated to be stable up to 100°C. and also stable in the anhydrous condition in air. It forms no hydrates. It was ground to a fine powder, sieved through a 100 mesh B.S. sieve, and the fraction passing the sieve dried under vacuum at 10^{-4} mm. of mercury pressure for two hours at 80°C. The material was transferred to the dry box and loaded as for potassium carbonate. The heat of solution of this material was measured at various concentrations up to approximate saturation.

(*c*) *Ferrous Oxalate Dihydrate*

The material available was of laboratory reagent quality. The solubility of this salt is given in the *Handbook of chemistry and physics*, 30th edition, as 0.022 gm. per 100 ml. at room temperature, with a very small temperature dependence. The material was dried by pumping *in vacuo* for two hours at room temperature and loaded under dry box conditions. In working out the total molar heat of solution, the amount of solute was taken from the above solubility figure.

*"*Tufnol" is a plastic material made from laminated cloth bonded with a water-insoluble heat-setting resin.*

†*British Pharmacopoeia.*

(*d*) *Ammonium Hypophosphite*

The material available was of laboratory reagent quality. In the first trials, it was ground to a powder and dried by pumping *in vacuo* at 80°C. for two hours in a platinum crucible. This treatment caused considerable darkening of the material due, presumably, to the presence of small amounts of some impurity. For subsequent experiments, it was evacuated at room temperature to dry it. It was loaded under dry box conditions.

(*e*) *Sodium Hypophosphite*

The material available was of B.P. quality, and on analysis proved to be substantially the anhydrous salt. The small residual moisture was removed by evacuation at 100°C., yielding the anhydrous material which was thereafter handled under dry box conditions as for potassium carbonate.

(*f*) *Hydrazine Mononitrate*

The material available was a white, crystalline solid of satisfactory melting point (70.5°C.). It was dried before use by pumping *in vacuo* for five to six hours at room temperature and keeping overnight in a vacuum desiccator over phosphorous pentoxide before loading under dry box conditions. Higher temperatures of drying were considered inadvisable because of the possibility of decomposition.

(*g*) *Barium Hypophosphite* (*Anhydrous*)

The material available was of laboratory reagent quality. After heating *in vacuo* at 80°C. for two hours, at 100°C. for one hour, keeping at atmospheric pressure of dry air at 110°C. overnight and a further three hours *in vacuo* at 80°C., it had attained constant weight and was taken as being anhydrous and was then loaded under dry box conditions.

(*h*) *Barium Hypophosphite Monohydrate*

This was prepared by dissolving the previous material in boiling, distilled water, filtering to remove any carbonate, etc., and allowing it to crystallize at room temperature. The crystals obtained were filtered free of mother liquor, dried by crushing on a filter paper, and allowed to dry further by exposure to a current of dry air at room temperature. A sample of this material, on heating at 80°C. *in vacuo* to constant weight, lost 6.28% of its weight, indicating that it was substantially pure monohydrate; the formula $Ba(H_2PO_2)_2.H_2O$ requires a loss in weight of 6.31%. The salt was used after this superficial air drying and loaded *directly* into the "Tufnol" pot *without* employing the dry box technique.

(*j*) *Sodium Permanganate Monohydrate*

The material available was the laboratory reagent, stated to be trihydrate. Sodium permanganate also forms a stable monohydrate. In order to prepare the pure monohydrate, the material was crushed to a fine powder, left *in vacuo* over phosphorus pentoxide overnight, then heated *in vacuo* for two hours at 80°C., followed by two hours at 100°C., after which constant weight had been attained. The loss in weight was 23.63%, calculated on the final weight. Pure trihydrate coming down to monohydrate would lose 23.53% of its weight,

calculated on the monohydrate weight. Dehydration to the anhydrous salt would involve a loss in weight of 38.09%, calculated on the weight of anhydrous material. This agreement between the experimental and calculated figures was evidence that the original material *was* trihydrate, and that the material obtained after the above treatment was monohydrate. It was loaded into the "Tufnol" pot under dry box conditions.

(*k*) *Sodium Permanganate Trihydrate*

This material was used as supplied, crushed to a fine powder, and loaded directly into the "Tufnol" pot without the use of the dry box technique.

(*l*) *Pentaerythritol*

The material supplied was a pure, white compound of satisfactory melting point (255°C.) which had been recrystallized from water. It was dried superficially by storage over phosphorus pentoxide in a vacuum desiccator for 60 hr. It was loaded under dry box conditions.

The general principles of adiabatic calorimetry are well enough established and the details of technique used in this investigation did not differ substantially from those employed in a similar investigation with fibers (Bright and Carson (2)). In determining the heat of solution of a material which gave a cooling effect, electrical energy in known amount was supplied to give a net heating and thereby a close approximation to adiabaticity was retained. A typical experimental time/temperature plot for such a determination is shown in Fig. 2. At the start of the investigation of each fresh material, a short trial experiment was always carried out to determine the sign and order of magnitude of the heat of solution. If exothermic, no further precautions were necessary; if endothermic, the amount of solute was chosen so that, when it was added against the supply of electrical energy, a resultant rise of temperature was assured in the actual experiments used to give the finally accepted values for the heats of solution. The heats of solution were always worked out in kcal./mole; the conversion factor 1 watt-min. = 14.335 gm-cal. was used throughout. The concentrations were expressed either directly as percentages by weight or inversely, as dilutions, as the number of moles of water per mole of solute.

EXPERIMENTAL RESULTS

The results obtained for potassium carbonate (anhydrous) are given below, along with the figures calculated from Berthelot and Ilosvay's equation (1), quoted above, neglecting differences of concentration.

The agreement between the calculated and experimental figures is considered to be an adequate justification for the use of the present experimental tech-

Mean temperature of experiment (°C.)	Molar dilution (moles H_2O per mole K_2CO_3)	Calculated heat (kcal./mole) $-\Delta H$	Experimental heat (kcal./mole) $-\Delta H$
26.5	553	7.35	7.08
27.7	605	7.44	7.20
29.9	541	7.60	7.47

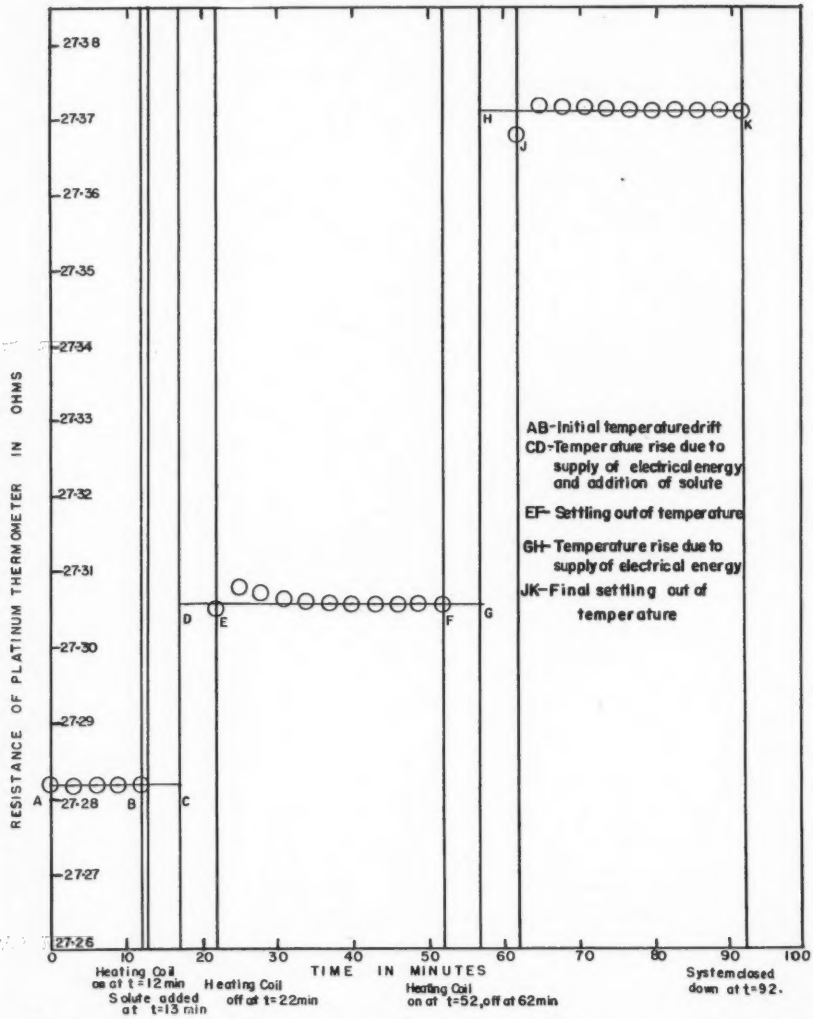

FIG. 2. Typical calorimetric run with endothermic heat of solution, solute—pentaerythritol.

nique, particularly when it is remembered that no account is taken here of the different dilution to which Berthelot and Ilosvay's equation (1) is intended to apply (100 moles H_2O/mole K_2CO_3).

The following figures were obtained for the heat of solution of ferrous oxalate dihydrate in water to produce a saturated solution:

(i) $-\Delta H = 0.93$ kcal./mole (29.0°C.),
(ii) $-\Delta H = 1.03$ kcal./mole (29.1°C.).

The molar dilution of a saturated solution is of the order of 4500 moles of water per mole of solute. This figure for the heat of solution can be approximate only since the gross amount of heat liberated was so small, but it indicates that the true value of the heat of solution at infinite dilution is of the order of $-\Delta H_\infty = 1$ kcal./mole.

The experimental heats of solution of the remaining materials are given in Table I, and the heats of solution at infinite dilution obtained by extrapolation of the line through the experimental points to zero concentration. To calculate the heats of dilution, if required, it was more convenient to cast the results in slightly different form. Thus in Table II, are given the heats of solution at various dilutions expressed as moles of water per mole of solute. These figures are smoothed values taken from suitable graphs drawn through the experimental points. These graphs are shown in Fig. 3.

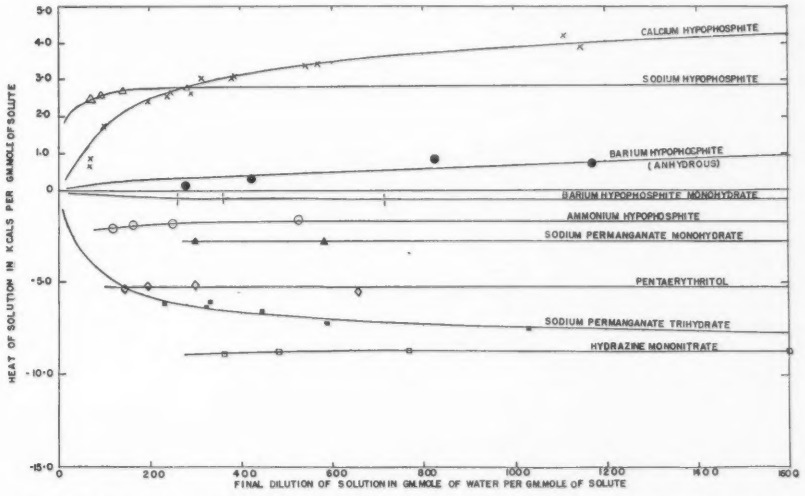

FIG. 3. Variation of heat of solution of solutes with the final dilution of the solution. (N.B. Vertical scale for exothermic heats is more extended than for endothermic heats.)

DISCUSSION

Some discussion of the sources and magnitudes of error involved is appropriate. One of the most likely errors is in the preparation of the salt in a reproducibly dry condition and in maintaining it in this condition up to the moment of release into the water. If the figures in Table II are plotted as graphs (see Fig. 3) it will be seen that the first additions of water to a saturated solution of the highest hydrate, or of the anhydrous material if no hydrate be formed, produce the greatest thermal effects per unit quantity of *water*, i.e. the slope $d(-\Delta H)/dD$, where $-\Delta H$ is the heat of solution and D the dilution, is greatest numerically as $D \rightarrow 0$. Thus, small amounts of residual moisture can make relatively large errors in the measured heats of solution in those cases where measurements are being made in the more concentrated solutions.

TABLE I

EXPERIMENTAL RESULTS FOR HEATS OF SOLUTION

Substance investigated	Mean temperature of experiment (°C.)	Concentration of solute (% by weight)			Final molar dilution in moles water per mole solute	Differential molar heat of solution ($-\Delta H$) in kcal. per mole of added solute	Extrapolated heat at infinite dilution ($-\Delta H_\infty$)
		Initial	Final	Mean			
	28.3	0	0.82	0.41	1147	+3.86	
	32.3	0	0.85	0.42	1110	+4.21	
	28.4	0	1.63	0.82	570	+3.43	
	29.3	0.85	1.71	1.28	543	+3.36	
Calcium hypophosphite	29.3	1.65	2.41	2.03	382	+3.02	
$Ca(H_2PO_2)_2$	29.0	1.71	2.40	2.05	384	+3.08	
	28.7	2.40	2.94	2.67	312	+3.03	
	28.3	2.41	3.15	2.78	290	+2.62	+4.20
	29.1	2.94	3.72	3.33	245	+2.68	
	28.2	3.15	3.87	3.51	235	+2.55	
	28.5	3.87	4.62	4.25	195	+2.43	
	28.8	7.41	8.55	7.98	101	+1.70	
	28.7	8.55	8.83	8.69	98	+1.74	
	28.9	12.00	12.42	12.21	67	+0.84	
	28.9	12.42	12.60	12.51	66	+0.66	
	29.0	0	0.87	0.43	526	−1.64	
Ammonium hypophosphite	28.9	0.87	1.81	1.34	250	−1.83	
$NH_4.H_2PO_2$	29.4	1.81	2.77	2.29	162	−1.93	−1.60
	28.9	2.77	3.69	3.23	120	−2.09	
	28.9	0	1.70	0.85	283	+2.79	
Sodium hypophosphite	29.0	1.70	3.36	2.53	141	+2.70	
$Na.H_2PO_2$	29.0	3.36	4.97	4.16	93	+2.59	+2.88
	29.1	4.97	6.56	5.76	70	+2.48	
	29.6	0	0.328	0.164	1601	−8.77	
Hydrazine mononitrate	29.1	0.328	0.682	0.505	767	−8.72	
$N_2H_4.HNO_3$	29.7	0.682	1.078	0.880	484	−8.76	−8.72
	29.2	1.078	1.434	1.256	363	−8.87	
Barium	28.7	0	1.250	0.625	1171	+0.72	
hypophosphite	29.0	1.804	3.380	2.592	424	+0.30	
(anhydrous)	28.9	3.380	5.048	4.214	279	+0.11	+1.05
$Ba(H_2PO_2)_2$	28.8	0	1.924	0.962	827	+0.82	
Barium hypophosphite	28.7	0	2.172	1.086	713	−0.48	
monohydrate	28.9	2.172	4.212	3.192	360	−0.43	−0.53
$Ba(H_2PO_2)_2.H_2O$	28.9	4.212	5.746	4.979	260	−0.42	
Sodium permanganate	29.0	0.64	1.49	1.07	586	−2.79	
monohydrate	29.2	1.49	2.87	2.18	300	−2.78	−2.80
$NaMnO_4.H_2O$							
Sodium	29.0	0	1.04	0.52	1031	−7.50	
permanganate	29.5	0	1.81	0.90	590	−7.17	
trihydrate	28.8	1.04	2.37	1.71	447	−6.56	−8.08
$NaMnO_4.3H_2O$	29.1	1.81	3.25	2.53	323	−6.33	
	29.0	2.37	3.16	2.77	333	−6.05	
	28.9	3.25	4.47	3.86	232	−6.11	
	29.2	0	1.134	0.567	656	−5.48	
Pentaerythritol	30.1	1.134	2.485	1.809	299	−5.17	−5.28
$C(CH_2OH)_4$	28.8	2.485	3.815	3.150	195	−5.25	
	29.0	3.815	5.188	4.501	143	−5.34	

TABLE II

SMOOTHED VALUES OF HEATS OF SOLUTION ($-\Delta H$) GIVEN IN KCAL./MOLE OF SOLUTE IN x MOLES OF WATER
(No account has been taken of temperature variation)

Substance	$x = 50$	100	200	300	400	600	800	1000	1200	1400	1600	∞
Calcium hypophosphite	+0.95	+1.70	+2.50	+2.93	+3.14	+3.45	+3.69	+3.90	+4.04	+4.15	+4.20	+4.20
Ammonium hypophosphite	—	−2.20	−1.84	−1.78	−1.72	−1.70	−1.68	−1.66	−1.64	−1.62	−1.61	−1.60
Sodium hypophosphite	+2.37	+2.60	+2.73	+2.80	+2.82	+2.83	+2.84	+2.85	+2.85	+2.86	+2.86	+2.88
Barium hypophosphite (anhydrous)	+0.11	+0.20	+0.28	+0.35	+0.40	+0.47	+0.57	+0.68	+0.80	+0.87	+0.92	+1.05
Barium hypophosphite (monohydrate)	−0.20	−0.30	−0.40	−0.43	−0.45	−0.47	−0.49	−0.50	−0.51	−0.52	−0.53	−0.53
Sodium permanganate (monohydrate)	—	—	—	−2.80	−2.80	−2.80	−2.80	−2.80	−2.80	−2.80	−2.80	−2.80
Sodium permanganate (trihydrate)	−3.30	−4.67	−5.80	−6.30	−6.68	−7.06	−7.32	−7.50	−7.58	−7.67	−7.73	−8.08
Hydrazine nitrate	—	—	—	−8.90	−8.82	−8.76	−8.75	−8.74	−8.73	−8.73	−8.72	−8.72
Pentaerythritol	—	−5.28	−5.28	−5.28	−5.28	−5.28	−5.28	−5.28	−5.28	−5.28	−5.28	−5.28

The calorimetric errors depended chiefly upon the reliability of temperature extrapolations. A study of the plots for the various experiments (such as that shown in Fig. 2) leads to the conclusion that the extrapolations involved in the determination of these temperature changes are reliable to within ±0.001°C., irrespective of the magnitude of the rise involved. Thus, the measurements of the numerically lowest heats probably carried an error of approximately ±10%, while those of the higher figures, which comprise the majority of the determinations, carried an error of not greater than ±0.2 to 0.5%, corresponding to an error of 0.01 to 0.025 kcal./mole on a figure of 5 kcal./mole.

The errors introduced by the salt not being perfectly dry at the time of solution cannot readily be assessed, but from the nature of the error, they tend to produce numerically low results. Thus, in drawing the various curves, from which the figures given in Table II are taken, if less weight is given to the points lying obviously numerically low, then the resulting curve is more likely to represent the true figures. The adoption of such a procedure leads to the conclusion that the final figures given in Table II are accurate in the majority of cases to within ±0.01 to 0.02 kcal./mole.

In several cases, experimental measurements were not available for the more concentrated solutions and Table II could not be completed within that range. On theoretical grounds, all these figures should tend to zero for zero *dilution* since the addition of small quantities of water to the solid materials is accompanied by very little thermal effect per mole of *solute*. Near zero dilution, however, discontinuities will occur in the curve of heat of solution against dilution, corresponding to the formation of saturated solutions and of any hydrates which the material in question may possess. Nevertheless, at *zero* dilution, the heat effect per mole of solute must be zero. According to the Debye-Hückel theory, heat should always be evolved in the dilution of a dilute solution of an electrolyte. In more concentrated solutions, however, where the simple theory does not hold, the heat effect of dilution may be of either sign. Thus, the curve of heat effect against dilution may or may not approach the value for infinite dilution without a point of inflection. Indeed, experimental evidence quoted in Bichowsky and Rossini's tables (*loc. cit.*) shows that there very often *is* a point of inflection (e.g. sodium, ammonium, and barium chlorides) although the dilution range at which this occurs varies widely from one substance to another. It is largely a matter of balancing the heat evolved in the hydration of the ions against the energy required to separate them to greater distances than those at which they occur in the crystal lattice and in concentrated solutions.

ACKNOWLEDGMENTS

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SOME MECHANICAL FEATURES OF A PLATE-TYPE HTST PASTEURIZER[1]

By S. A. Hansen,[2] F. W. Wood,[3] and H. R. Thornton[4]

ABSTRACT

A 1000 lb./hr. commercial plate-type HTST pasteurizer with a 15-sec. holding tube was subjected to study before and after a rearrangement of the plates in the heating section. Time–temperature curves for the entire process are given. Air pockets in a downward-sloping holding tube decreased the holding time by as much as 50%. Holding time on diverted flow was approximately two seconds less than on forward flow, as a restrictor fitting was not installed on the flow diversion line. The computation of milk flow rates was affected by water leaks past the diversion valve, lack of restrictor fitting on flow diversion line, plate arrangement, stabilization of water flow rate, air pockets, and variable milk–water ratios. The pasteurizing effect of the heating-up and cooling intervals is computed and the total pasteurizing effect of the process is shown to be approximately double that of the holding section alone. Attention is directed to the variable meaning of time in pasteurization time–temperature combinations. Some implications of these findings in public health control of this type of pasteurizer are discussed.

INTRODUCTION

A small, commercial, plate-type HTST (high-temperature short-time) pasteurizer recently installed in the laboratory of this department was studied experimentally. Canadian research on this type of pasteurization has been inadequate for the setting of public health standards and for control. It is hoped that the information set forth in this communication will add to our knowledge and aid in the ultimate establishment of sound HTST pasteurization procedures. Moreover, this type of apparatus permits precise time and temperature measurements at any desired point within the machine, which is an important consideration in phosphatase inactivation and bacterial thermal death studies.

METHODS

The experimental pasteurizer had a maximum capacity of 1000 lb./hr. and was equipped with accessories in common use on this continent, such as a Taylor model 39VJ1 flow diversion valve, and Taylor controls. A Waukesha positive displacement pump was installed between the regenerative and heating sections, and all pipelines, including the holding tube, were $1\frac{1}{2}$ in. O.D.

All flow time measurements, other than volume time, were made by the salt conductivity test patterned after the method first outlined by Fay and Fraser (5). In this test water is the flowing or processed liquid. Each trial run

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Contribution from the Department of Dairying, University of Alberta, Edmonton, Alberta.
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This investigation was supported by a grant from the National Research Council of Canada. Issued as paper No. 289 of the Canadian Committee on Food Preservation.
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[3] *Assistant Professor of Dairying.*
[4] *Professor of Dairying.*

with milk was preceded by such timing measurements. Initially, 14 gauge copper wire electrodes, 2 mm. apart and 2 cm. long, as recommended by Jordan (6), were mounted in rubber stoppers fitted into openings at the upstream and downstream ends of the holding tube, the pasteurized milk entrance to the regenerative section, and the cold pasteurized milk outlet of the pasteurizer. Later, these electrodes were replaced, wherever possible, by the recommended 3A Standard type (3). No differences were observed in the results obtained with the two types of electrodes. On the assumption that maximum velocity of flow occurs at the center of the pipe, the electrodes at the downstream end of the holding tube were centered as close as possible to the longitudinal axis of the pipe. For measuring flow times in the heating and regenerative sections, electrodes of 32 gauge sheet tin insulated with Minnesota Mining and Manufacturing Company electrical tape No. 33 were inserted between the plates. The saturated salt solution was injected manually in 40 ml. quantities through a spray-type nozzle to avoid impulsion of the solution in the direction of flow. All time intervals were measured manually with a stop watch.

Temperatures within the heating and regenerative sections were calculated from readings of copper and iron thermocouples held between the plates at a constant distance of 2 in. from the peripheral gaskets. Insulation was provided when required and care was exercised to minimize interference with liquid flow.

All thermocouples and indicating thermometers were calibrated against a thermometer graduated to 0.1°C. and certified to 0.01°C. by the Physics Division of the National Research Council of Canada. All temperatures reported are corrected to the nearest 0.1°F. on this basis.

Terms used conform to the following definitions:

Milk flow rate or water flow rate—pounds of milk or water delivered per hour. The milk or water delivered in a stop-watch measured time interval, usually five minutes, was weighed and the rate calculated as pounds per hour.

Time.—Unless otherwise stated, all times are in seconds and are for milk calculated by multiplying the time found with the salt test by the ratio $\frac{\text{water flow rate}}{\text{milk flow rate}} \times 1.032$ at the same pump settings.

Holding time—measured from the outlet of the heating section to the location of the indicating thermometer and controller bulb at the end of the holding tube.

Volume time—$\frac{\text{holding tube volume} \times \text{time}}{\text{milk volume delivered}}$.

Control time—time during which the milk was not below the control temperature.

Control temperature—indicating thermometer temperature at which the controls were set.

Heating-up and cooling equivalents—necessary time at control temperature for equivalent heat-treatment effect.

RESULTS

Air Pockets

In the initial installation a section of the holding tube sloped downward from the heating section outlet, in consequence of which air was entrapped in the tube and the holding time decreased by up to 50%, depending on the amount of air entrapped. Normal holding times could be restored by bleeding off the air through a valve installed at the highest point of the tube. Subsequent modification of the holding tube provided a continuous, gradual rise or upward slope from the heating section outlet to a location downstream from the flow diversion valve. When the pasteurizer was then operated at rated capacity, the holding times varied between 15 and 16 sec. The holding tube in each installation was designed by the manufacturer for 15-sec. holding.

The plate sections and certain of the pipeline accessories also offer opportunities for air collection and these air pockets may shorten the pasteurizing time exclusive of the holding time. When milk enters a plate section at the bottom, the air is forced out of the exit at the top and no air pockets form

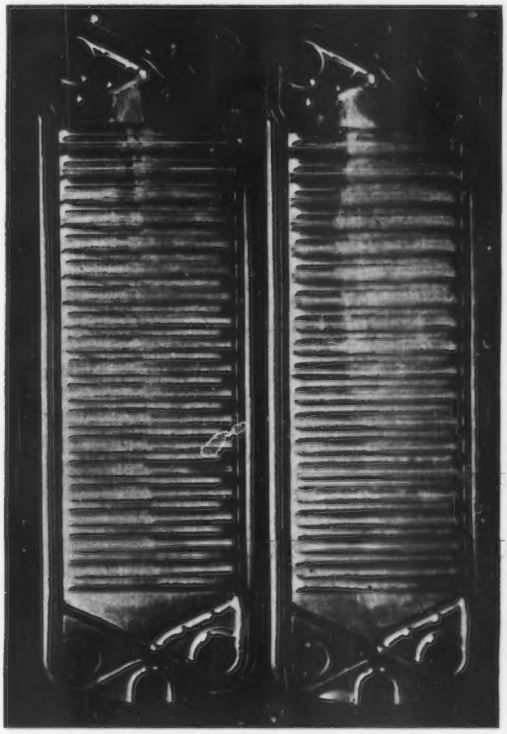

FIG. 1. Plates from the heating section showing the "baked-on" effect of entrapped air.

between the plates. On the other hand, when the milk enters the plate section at the top, an air pocket forms between the plates contiguous to the milk inlet. Thermocouple measurements showed that temperatures in such foam-filled spaces differed from those in nearby milk-filled spaces by as much as 38°F. and tended to approximate that of the heatant. When the milk entered the plate section at the bottom and filled the entire space between the plates, temperatures at any one horizontal level were essentially identical across the plates.

A deposit of milkstone forms on the plates in contact with the air or foam pocket. This is illustrated in Fig. 1 which is a photograph of the first two plates in plate arrangement B of the heating section, the milk inlet of which is at the top of the plates. For photographic purposes the accumulation was allowed to gather for a considerable period of time. An examination clearly reveals two areas, the area in which the milk solids were "baked on" by the excessive heat and the relatively clear area, presumably kept so by the turbulence of the flowing liquid.

Flow Diversion Valve

The flow diversion valve has a milk-tight but ungasketed diversion port which permits leakage when water is being processed. This leakage was observed to be as high as 2.5% of the total flow and was collected and added to the regular flow in all water flow rate measurements. Neglect of this factor would decrease the calculated milk holding time by as much as one-half second.

Stabilization of Flow Rates

When water was being processed, a gradual capacity decrease was observed until a point of stability was reached. Table I shows typical results of five trials at differing pasteurizer adjustments and pump settings. Except for special purposes, no timing measurements were made, therefore, during a preliminary stabilization period of not less than 30 min. of operation. While no attempt was made to determine the cause of this initial diminishing rate of flow, a plausible explanation is the accumulation of air in such places as the upper spaces of the plate sections downstream from the pump until an equilibrium between air and liquid is established.

TABLE I

STABILIZATION OF WATER FLOW RATES

Minutes	Trial				
	1	2	3	4	5
5	810	942	906	834	960
11	804	930	876	824	942
18	798	930	876	822	924
24	792	930	876	816	924
31	792	924	876	816	918
43	792	924	—	816	936

Plate Arrangements

After the pasteurizer was modified to permit upward sloping of the holding tube, two plate arrangements, A and B, were studied. Plate arrangement B resulted in enlarged heating and reduced regenerative sections, the net effect of which is to be observed in Figs. 2 and 3 and may be measured in differing time–temperature combinations despite identical holding times (Table III).

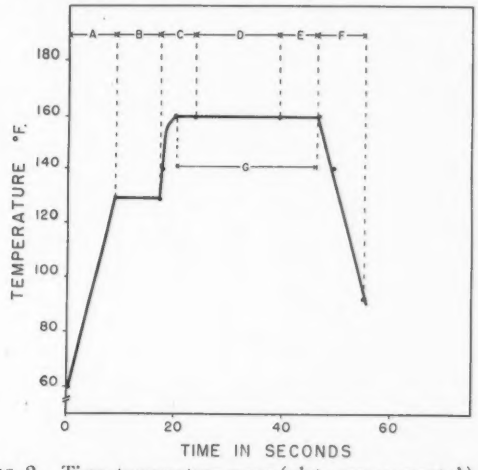

FIG. 2. Time–temperature curve (plate arrangement A).
A—regenerator
B—filter
C—heater
D—holder
E—holder to regenerator
F—regenerator
G—control time

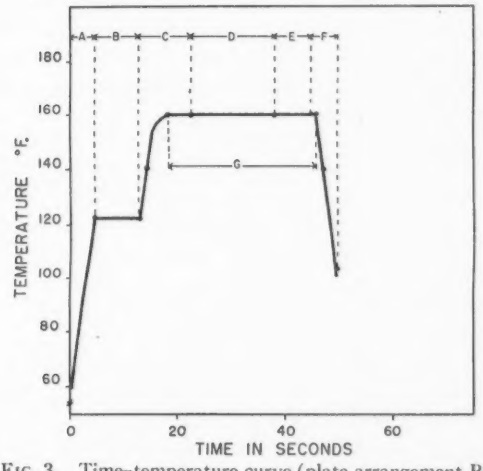

FIG. 3. Time–temperature curve (plate arrangement B).
A—regenerator
B—filter
C—heater
D—holder
E—holder to regenerator
F—regenerator
G—control time

Holding Time on Diverted Flow

The pasteurizer was not equipped with a diversion line restrictor fitting, which during diverted flow would compensate for the normal head pressure of the regenerative and cooling sections. The data of Table II are of three consecutive measurements of the diverted flow at the same pasteurizer adjustment and indicate that the holding time during diversion is approximately two seconds less than during forward flow.

TABLE II

THE EFFECT OF DIVERSION ON HOLDING TIME IN SECONDS

Direction of flow	Test		
	1	2	3
Forward	15.5	15.5	15.5
Diverted	13.8	13.3	13.4
Difference	1.7	2.2	2.1

Flow Rate Ratios

During the course of the study comparative water and milk flow rates were measured and the latter were invariably found to be higher. Under operational conditions giving the same water flow rate the milk flow rate was not uniform, the percentage increase over water varying from a low of 10.4 to a high of 21.1. Weber (10) attributes such fluctuations to variations in line voltage, pressure applied to the exchanger plates, and air leaks on the suction side of the pump. It is probable that in the small pasteurizer under study air leaks at the gasketed edges of the plates were a major cause of these variations because gasket length per unit volume of liquid is greater than in large machines.

The speed of the pump also influenced the milk–water ratio in that at high pump speeds the percentage increase was low, while it was high at low pump speeds. The difference in viscosity between milk and water with attendant differences in pump slippage provides an explanation for these variations.

In 75 "normal" operations of the pasteurizer with differing water flow rates, the milk–water ratio increases varied from a low of 3.7% to a high of 21.1%. These figures are similar to the results of Weber who reported increases from 0 to 25%.

Internal Temperatures and Times

Although milk flow rates differed from water flow rates, as measured by the amount delivered per unit of time, no difference was discernible as measured by temperatures at specified points between the plates. Both milk and water reached the control temperature at the same place in the heating section.

Table III gives the length of time for which the milk was at control temperature in each section of the apparatus for each of the two plate arrangements and facilitates interpretation of Figs. 2 and 3. These results are very similar

to those of Ashton (1). The temperature drop between the exit of the heating section and the inlet of the regenerative section was less than 0.1°F.

It is to be observed in Table III that with plate arrangement A the control time was 26.5 sec. and with plate arrangement B, 27.8 sec., although the holding times were identical. It is important to recognize that the so-called holding time in this pasteurizer is only a little over 60% of the total time for which the milk is at the pasteurizing temperature. Equivalent measurements

TABLE III

THE NUMBER OF SECONDS AT CONTROL TEMPERATURE IN THE PASTEURIZER SECTIONS

Section	Plate arrangement	
	A	B
Heating	3.5	4.2
Holding	15.7	15.8
Holding to regenerative	7.0	7.0
Regenerative	0.3	0.8
Total	26.5	27.8

for a large capacity commercial pasteurizer show a holding time which is 67% of the total time. This difference between the experimental and commercial pasteurizers is accounted for in part by the fact that the flow diversion valve and thermometer tees were the same size in the former as in the latter machine but acted as expansion chambers with lessened flow rate only in the experimental apparatus.

Heating-up and Cooling Equivalents

It has long been recognized that the heating-up and cooling periods contribute to the total pasteurizing effect. A great deal of effort has been expended on apparatus designed to minimize this factor by very rapid heating and cooling. Sometimes this has been accomplished at the sacrifice of more important features.

Ball (2) suggested mathematical formulas for computing this effect in canning sterilization procedures. The appropriate formulas were applied in the present study with apparent success. Scrutiny of Figs. 2 and 3 reveals that temperatures rise logarithmically in the heating section and fall linearly in the significant part of the regenerative section. The time required to reach the control temperature and to cool to below effective pasteurizing temperatures varies with the control temperature. The heating-up equivalent at 160°F. as computed by the Ball method was 2.0 sec. with plate arrangement B and the cooling equivalent for the same control temperature was 0.2 sec. Thus, in any consideration of the total pasteurizing effect in this apparatus at 160°F., 2.2 sec. must be added to the total time for which the milk is at the control temperature.

Confidence in the soundness of this type of application of the Ball method is heightened by certain empirical evidence which indicated that the total equivalent at 160°F. could not be greater than three seconds. This aspect will be further exploited in a subsequent communication.

The Variable Meaning of Time

In this type of study two methods have been used for measuring time, viz.,

1. the salt, or other equivalent, method,
2. the volume method.

The first method is that usually used for public health control of HTST pasteurizers and is applied to the holding section. The time measured by this method approaches that of the fastest moving particle and the closeness of approach depends on the state of turbulence. Since bacterial flow follows molecular flow in a streaming liquid, it is the sounder time measure in thermal death considerations, although, ideally, fastest measured time and fastest particle time should coincide. For certain other purposes, such as in phosphatase inactivation studies, neither salt nor volume time has yet been shown to be completely adequate.

In this study the holding time of 15 sec. is 71% of the found volume time of 22.8 sec., which is within the general range of "efficiency of the holding tube or holding section" as reported by other investigators using various calculation methods (4, 7, 9).

Turbulence undoubtedly varies materially in different places within pasteurizers of this type but there are no reports of thorough investigations of this feature. Certain spaces would present difficulties, perhaps insurmountable, in such studies. However, the holding tube, which lends itself somewhat to turbulence measurements, has special significance inasmuch as most public health standards specify a holding time, which for enforcement must be measured. As turbulence increases, the difference between salt time and fastest particle time decreases, as does also the difference between salt time and volume time. Closer control then becomes possible for both bacterial thermal death time purposes and prevention of creaming impairment by over-pasteurization.

DISCUSSION

There is no purpose in specifying a holding time unless it is enforced. Holding tubes designed to meet the specification will only do so if air is not entrapped in the tube. Otherwise a shorter holding time will result. Many United States regulations provide against this possibility by specifying a holding tube sloped continuously upward from inlet to exit and this should be done in Canadian specifications. It has been reported to the authors (8) that too great a slope causes air bubbles to travel faster than the body of the milk in the tube but no data relative to this problem were found. It would seem sound, however, for the slope to be the minimum necessary for avoidance of air pockets.

Conceptions of the total pasteurizing effect of machines of this type should not be warped by the stress that has been laid on defined holding times. While

the total pasteurizing effect expressed as time at the pasteurizing temperature varies with the installation and probably to a small extent within any one installation with the operational conditions, it is always significantly greater than is indicated by the holding time. In the pasteurizer studied here the holding time was approximately 60% of the total time for which the milk was not below the pasteurizing temperature, and only 52.7% of the total pasteurizing effect, inclusive of the heating-up and cooling equivalents.

To conform to a temperature standard, it is necessary to set the flow diversion valve above the specified temperature. To avoid frequent cutting in and out of the flow diversion valve, it is necessary to set the controls above the flow diversion valve setting. Thus, the operational temperature in practice will be 1–1½°F. above the legal, specified temperature. This is an added safety factor frequently missing in conceptions of pasteurization by this type of apparatus.

In any continuous-flow apparatus used for such studies as phosphatase inactivation, time may have a variable meaning depending on measuring methods and this should not be ignored.

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PHOSPHATASE INACTIVATION IN HTST PASTEURIZATION OF MILK[1]

By S. A. Hansen,[2] F. W. Wood,[3] and H. R. Thornton[4]

ABSTRACT

Phosphatase inactivation was studied in a 1000 lb./hr. plate-type HTST pasteurizer, normally equipped with a holding tube with rated "holding time" of 15 sec. The pasteurizer with normal holding tube inactivated phosphatase to the 2 unit/0.5 ml. milk (4 p.p.m. phenol) end point when the control temperature was 157.7°F. The inactivation time (the total time that the milk was not below the control temperature plus the heating-up and cooling equivalents computed by the Ball method) was 28.7 or 30 sec. depending on the plate arrangement. This is approximately double the rated "holding time." When the control temperature was 160°F., the inactivation time was 16.8 sec. and the "holding time" was 9.6 sec. When the milk flow rate was increased to 60% above normal, phosphatase was inactivated at 159.7°F. with a "holding time" of 10.85 sec. The Ball method of determining the heating-up and cooling equivalents was empirically shown to be reasonably accurate for the particular heating-up and cooling intervals found. Inactivation was studied between 151.3°F. and 164.1°F. and the inactivation times when plotted on semilogarithmic paper follow a straight line having a Z value of 9.7°F. Rate of inactivation curves at two temperatures are given and do not support the view that the enzyme inactivation is strictly a first order reaction. The discussion includes some of the reasons for the inharmonious findings of various students of this problem. The exact time–temperature combinations required for phosphatase inactivation in milk not yet having been established, consideration is given to the difficulties of their determination as affected by the variable meaning of time.

INTRODUCTION

The practical control of HTST (high-temperature short-time) pasteurization by the phosphatase test assumes a precise knowledge of the time–temperature requirements for the inactivation of the enzyme in this temperature range. That the accurate determination of these requirements is fraught with difficulty, currently insurmountable, is illustrated in Table I which shows the discordant results of various investigators. Any furtherance of knowledge in this field is, therefore, worth while.

A small capacity plate-type HTST pasteurizer in this laboratory was undergoing investigation (4) and a concurrent study of phosphatase inactivation within the apparatus was deemed advantageous.

METHODS

The milk, ranging from 2.7 to 4% in fat content, was supplied from the raw milk storage tank of a city milk plant.

The pasteurizer, the two plate arrangements A and B, the timing and temperature measurements, and the definitions of terms are as previously detailed

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This investigation was supported by a grant from the National Research Council of Canada. Issued as paper No. 290 of the Canadian Committee on Food Preservation.
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TABLE I

PHOSPHATASE INACTIVATION CHARACTERISTICS ACCORDING TO VARIOUS AUTHORITIES

Authority	Seconds for inactivation at 160°F.	*Z* in °F. of inactivation curve	Inactivation end point, p.p.m. phenol
Hetrick and Tracy (5)	35.9	8.90	1
Sanders and Sager (12)	24.0	8.73	4
Holland and Dahlberg (6)	20.4	8.35	40
Lear and Foster (10)	16.8	8.82	0.5

(4). Milks 1 to 10 were heat-treated by plate arrangement A and the remaining milks by plate arrangement B.

The processing temperature was varied by raising the control temperature gradually through the desired range and sampling time was governed accordingly, since precise times were known throughout the entire apparatus.

Holding times were controlled either by varying the length of the holding tube or, as in one series of experiments, by varying the pump speed. The "normal" holding tube had a rated holding time of 15 sec. but this was found to vary within the range 15–16 sec. when the pasteurizer was operated at rated capacity. The control time was the total time, measured by the salt test, during which the milk was not below the control temperature. The inactivation time was the control time plus the heating-up and cooling equivalents.

The samples for the phosphatase tests were taken at the milk outlet of the cooling section at 40–50°F. and were stored at 40°F. until they were tested on the following day.

Phosphatase was determined by the technique of Sanders and Sager (11) as accepted by the Association of Official Agricultural Chemists (2). Color transmission was measured in 10 ml. tubes at 600 mμ. with an Evelyn photoelectric colorimeter. The quantities of phenol, after subtraction of control values, were read directly from a standard transmission–concentration curve prepared with known amounts of phenol. Phosphatase was considered to be inactivated at a phenol level of 2 μgm. per 0.5 ml. of milk, which is equal to 4 p.p.m. of phenol. Phosphatase activity is expressed as Sanders and Sager units of phosphatase in 0.5 ml. milk rather than as p.p.m. of phenol and, thus, 2 units means 2 units/0.5 ml. milk.

RESULTS

Inactivation during Various Heat-treatments

The residual phosphatase units after heat-treatment at temperatures within the range 156.3–160.1°F. are given in Table II. The temperature of inactivation for each milk as shown in the last column of the table was obtained by plotting the residual phosphatase values on semilogarithmic paper and determining the temperature at which the residual was 2 units. These data show that phosphatase was inactivated at an average temperature of 157.7°F. in an average holding time of 15.65 sec. The average control time was 27 sec. and the average inactivation time was 29.2 sec.

TABLE II

RESIDUAL PHOSPHATASE UNITS AFTER VARIOUS HEAT-TREATMENTS

Milk	Holding time, sec.	Temperature, °F.																Inactivation at °F.
		156.3	156.5	156.8	157.0	157.3	157.5	157.8	157.9	158.3	158.5	158.7	159.0	159.2	159.6	159.7	160.1	
1	15.2	7.24		4.50		2.43		1.76		0.71		0.71		0.04		0.14		157.6
2	15.3	>8.00		7.20		4.24		2.44		1.28		0.76		0.28		0.29		158.0
3	15.9	7.34		5.00		2.48		1.56		0.68		0.60		0.72		0.20		157.5
4	15.4	>8.00		6.48		4.40		2.68		1.27		0.72		0.74		0.60		158.0
5	15.7	7.24		5.20		2.52		1.72		0.56		0.00		0.24		0.00		157.6
6	15.7	4.27		3.16		2.11		1.48		0.59		0.00		0.00		0.00		157.4
7	15.9	7.68		4.68		2.88		1.72		1.26		1.08		0.52		0.52		157.7
8	15.7	5.76		3.20		2.12		1.28		0.52		0.76		0.00		0.00		157.4
9	15.3	>8.00		7.13		3.96		2.40		1.48		1.24		0.96		0.96		158.0
10	15.8	>8.00		7.20		2.96		1.60		1.06		0.50		0.45		0.18		157.6
19	15.9		5.16		3.24		2.00		1.32		0.72		0.62		0.28		0.24	157.5
20	16.0		8.04		3.94		2.16		1.52		0.68		0.48		0.36		0.18	157.6
28	15.2		8.92		5.12		3.08		1.76		0.96		0.68		0.61		0.49	157.8
29	15.1		8.08		5.12		2.88		2.12		1.00		0.80		0.56		0.48	158.0
30	16.1		5.88		4.04		2.40		1.64		1.02		0.92		0.71		0.56	157.7
31	16.1		5.88		3.52		2.12		1.32		0.96		0.71		0.26		0.20	157.6
Average	15.65	—	6.99	5.18	4.16	3.01	2.44	1.86	1.61	0.94	0.89	0.64	0.70	0.40	0.46	0.29	0.36	157.7

By altering pump speeds the milk flow rate was increased by amounts up to 60% above the normal or rated capacity. The inactivation temperatures are plotted against these increases in Fig. 1 in which inactivation is seen to have taken place during the period of maximum flow rate at 159.7°F. when the holding time was only 10.85 sec. Control times were not measured.

By altering the length of the pipeline connecting the heating section outlet to the regenerative section inlet, the control time was varied over the range 10.9 to 79.2 sec. Table III, which summarizes the results of these experiments,

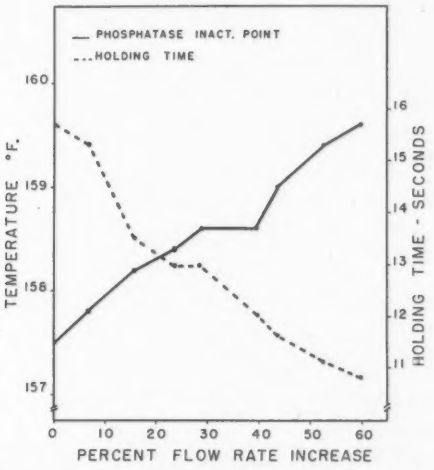

FIG. 1. Effect of flow rate increase on time–temperature requirements for phosphatase inactivation.

includes also each inactivation time, which is the sum of the control time and the heating-up and cooling equivalents. That is, had the pasteurizer heated and cooled the milk instantaneously, phosphatase would have been inactivated in 13.1 sec. at 160.7°F., or in 79.9 sec. at 153.3°F., time being measured by the salt test.

The Inactivation Curve

The time required to raise the temperature of milk from 143°F. to a control temperature of 160°F. was 3.1 sec., about 75–80% of which was between 153°F. and 160°F., and the time required to cool over the same range was 0.8 sec. It is recognized that some inactivation of phosphatase occurs during these processes and that the rate of inactivation increases with temperature. Time–temperature curves (4) near the control temperature are logarithmic during the heating-up period and linear during cooling. Table III shows that it requires about 80 sec. for inactivation at 153.3°F. Therefore, the inactivating effect of the heating-up and cooling treatments when the control temperature is 160°F. must be considerably less than the effect of the 3.9 sec. at 160°F. mentioned

TABLE III

TIME–TEMPERATURE REQUIREMENTS FOR INACTIVATION

Milk	Control time, sec.	Inactivation at °F.	Heating-up equivalent		Cooling equivalent		Inactivation time, sec.
			Sec.	%*	Sec.	%*	
11	10.9	160.7	2.0	15.47	0.19	1.46	13.1
12	10.9	160.7	2.0	15.47	0.19	1.46	13.1
13	17.2	159.5	1.6	8.27	0.19	1.08	19.0
14	17.3	159.2	1.5	8.27	0.19	1.09	19.0
15	18.9	159.3	1.5	7.06	0.19	1.01	20.6
16	19.3	159.7	1.7	7.96	0.19	0.97	21.2
17	23.6	158.7	1.2	4.88	0.19	0.79	25.0
18	23.9	158.7	1.2	4.83	0.19	0.78	25.3
19	28.2	157.5	0.9	3.18	0.19	0.71	29.3
20	28.5	157.6	0.9	3.14	0.19	0.70	29.6
21	38.3	156.1	0.7	1.78	0.19	0.51	39.2
22	38.7	156.2	0.7	1.76	0.19	0.53	39.6
23	60.9	154.6	0.6	0.95	0.19	0.32	61.7
24	61.5	154.7	0.6	0.93	0.19	0.31	62.3
25	73.3	154.0	0.5	0.71	0.19	0.28	74.0
27	79.2	153.3	0.5	0.58	0.18	0.23	79.9

**Expressed as percentage of inactivation time.*

above. For computation purposes 143°F. was chosen as the minimum temperature below which no significant destruction takes place. This was found to be a sound assumption inasmuch as the substitution of 153.3°F. for 143°F. resulted in insignificant differences in the computed heating-up and cooling equivalents.

The appropriate equations of Ball (3) were applied for the computation of the heating-up and cooling equivalents. The data in Table III disclose that the inactivating effect of heating-up, whether expressed as equivalents or as percentages of the inactivating time, becomes increasingly important with increasing control temperature. The cooling equivalents are of low magnitude but, when expressed as percentages of the control time, are seen also to become of increasing importance with increasing control temperature.

To procure the data in Table III, control temperatures varied within the range 151.3–164.1°F. Phosphatase was not inactivated in 80 sec. at temperatures below 153.3°F. and was inactivated in less than 10.9 sec. at temperatures above 160.7°F. Control times beyond these time limits were not studied. When plotted semilogarithmically, the inactivation times fall on a straight line (Fig. 2) which has the equation, $T = 171.84 - 9.66 \log t$, where T = temperature in °F. and t = time in seconds. The Z value is 9.7°F. and phosphatase is shown to be inactivated in 16.8 sec. at 160°F.

That it is misleading to disregard inactivation during the heating-up and cooling periods is illustrated by the fact that a similar plot of the control times only results in a curve which has a Z value of 8.9°F. and intersects the 160°F. coordinate at 15 sec.

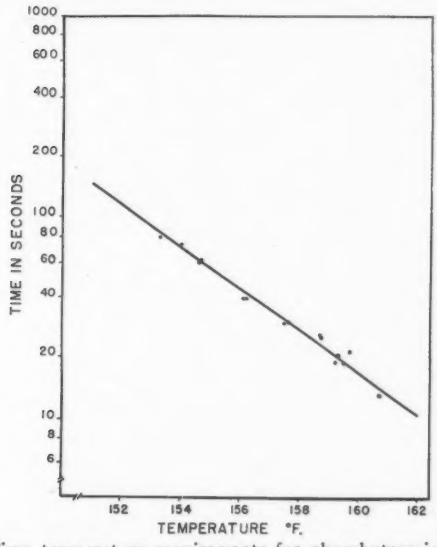

FIG. 2. Time-temperature requirements for phosphatase inactivation.

Rate of Inactivation

The results to follow confirm those of previous investigators (1, 5, 12) who are not in complete agreement with the view (8, 9, 14) that phosphatase inactivation not only follows a monomolecular law but is entirely a first order reaction.

The average residual phosphatase units of Table II, when plotted logarithmically, result in a straight-line curve until the residual is less than 1 unit of phosphatase. This is shown by examination of Fig. 3 which was constructed from the data for plate arrangement B. The data for plate arrangement A give a similar straight-line curve with a similar break.

It is apparent that inactivation of phosphatase is of logarithmic nature until a low residual is reached, after which inactivation is not logarithmic. A residual of 0.8–0.9 units represents an inactivation of 99.91–99.92%, assuming an original raw milk concentration of 1000 units (13). This phenomenon would not be encountered by those investigators who do not carry the inactivation into this region. Moreover, it was observed in the present studies that reproducibility in this region was not of a high order. Preliminary investigations indicate that the concentration of phosphatase is not constant in the milks of different cows. This variability tended to be minimized in the present studies by the use of pooled milk.

In determining rate of inactivation, temperature is constant and time is variable, while in Fig. 3 temperature is the variable. In Fig. 4 rate of inactivation data for a number of milks are plotted logarithmically for the two temperatures 158.5°F. and 160.1°F. over the phosphatase residual range 10–0.1 units. Again it is seen that in the region of low residuals the curves are not straight lines.

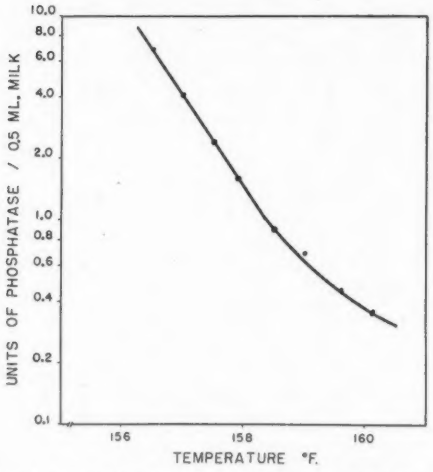

FIG. 3. Residual phosphatase units at various temperatures with "normal" holding time.

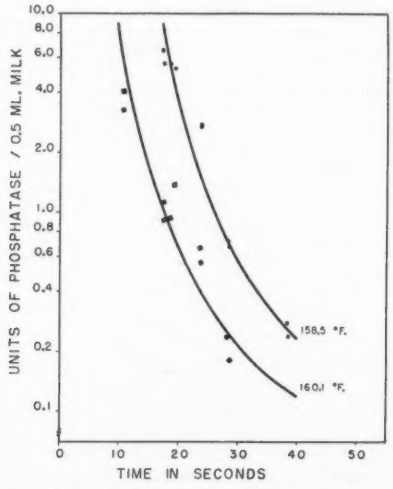

FIG. 4. Rate of phosphatase inactivation at 158.5°F. and 160.1°F.

Accuracy of Results

Residual phosphatase in each of two heat-treated milks was determined in replicate samples with the results reported in Table IV. It is seen that in this region of phosphatase concentration the phosphatase test itself had a reproducibility within approximately one unit.

The final column in Table II shows the over-all range of variability of results when uniform experimental technique was applied to different milks. The

TABLE IV

RESIDUAL PHOSPHATASE UNITS IN REPLICATE DETERMINATIONS

Milk	Replicate						Average	Range
	1	2	3	4	5	6		
A	4.20	3.32	3.32	3.32	4.06	3.84	3.68	3.32–4.20
B	3.96	3.42	3.16	2.84	3.32	3.08	3.30	2.84–3.96

inactivation temperatures varied between 157.4 and 158.0°F. and averaged 157.7°F. for each plate arrangement. Since the average control time with plate arrangement A was 26.5 sec. and with plate arrangement B 27.8 sec. (4) and the heating-up and cooling equivalents were constant, compensatory influences caused the average inactivation temperatures to coincide.

The variability of the milk flow rate – water flow rate ratio (4) is undoubtedly a partial cause of the variable holding times in Table II.

The variability of the phosphatase test replicates as shown in Table IV is of sufficient magnitude to cover the discrepancies, since a variability of 1 phosphatase unit is roughly equal to two seconds of time at the level of phosphatase concentration in question. The water timing measurements were much more sensitive than this, as reproducibility was within three-fifths of a second.

It is probable that the over-all accuracy of the time–temperature measurements, expressed as time, is of the general level of two to three seconds. The inactivation temperature, 157.7°F. (Table II), is probably reasonably close to the true mean, as it is an average.

The Variable Meaning of Time

By means of test-tube-in-water laboratory pasteurization in which tubes of milk were heated to 143°F. in one minute in water at 150°F., held in water at 143°F., and cooled to 90°F. in eight seconds in ice water, inactivation of phosphatase was found to occur in 33.8 min. This approximates the 37 min. at 143°F. found by Sanders and Sager (13). On the other hand when the curve in Fig. 2 is extrapolated into the LTLT (low-temperature long-time) pasteurization region, it intersects the 143°F. ordinate at approximately 16 min.

This apparent discrepancy arises partially from the differing principles governing timing measurements (4). In the holding tube of the plate-type pasteurizer the time measured by the salt method approaches that of the fastest particle, while volume time approaches average time. In the cell-type of heat-exchanger the time measured approaches average time, as does also the time measured by the salt method in turbulent continuous flow, an occurring condition in certain parts of a plate-type continuous heat-exchanger.

When corrections are applied for these and certain other not entirely imponderable variables the conflictions in Table I are lessened. Thus, Fig. 2 shows that phosphatase was inactivated at 160°F. in 16.8 sec. measured by the salt test. When put in terms of volume time, this becomes 23.5 sec. which is almost

identical with the 24 sec. found by Sanders and Sager, who used the same phosphatase unitage end point of inactivation but a cell-type holding section. The time measured by Hetrick and Tracy approached average time because of turbulent flow but the inactivation was carried to a higher degree. Inactivation to 4 p.p.m. phenol appears to have been effected by them at 160°F. in about 15 sec.

When a curve having a Z value of 9.7°F. and intersecting the 160°F. abscissa at 23.5 sec. is extrapolated into the LTLT region, it cuts the 143°F. abscissa at approximately 22 min. It is manifest that the precise inactivation characteristics of phosphatase are not yet established.

DISCUSSION

No heat-exchanger subjects all particles of milk to equal heat-treatment. For public health control the particle receiving the minimum heat-treatment is of paramount importance and, thus, in continuous-flow pasteurizers the salt test, or its equivalent, is the sound measure of time. For the exact determination of the time–temperature combinations necessary for phosphatase inactivation neither salt time nor average time is entirely adequate. The plate-type heat-exchanger with holding tube lends itself to accurate time and temperature measurements throughout the process but does not solve the problem of homogeneous heat-treatment.

In the present investigation the holding tubes were timed by the salt method at points close to the longitudinal axes of the tubes, the time measured approached fastest particle time, and the difference between salt time and volume time was relatively large. Volume time could not be determined for the other sections of the pasteurizer but their volume time – salt time ratios can be expected to be small because of turbulent flow. The samples for the phosphatase test were collected from the delivery end of the pasteurizer, were representative of average heat-treatment, and were, thus, mixtures of small volumes of milk varying in phosphatase concentration (7).

The pasteurizer equipped with the normal 15-sec. holding section and plate arrangement B inactivated phosphatase to the experimental end point at 157.7°F. in a total inactivating time of 30 sec. When the pasteurizer was controlled at 160°F. the total inactivating time was 16.8 sec. and the holding time was 9.6 sec. This, however, does not justify the general conclusion that phosphatase is inactivated at exactly 157.7°F. in 30 sec. or at 160°F. in 16.8 sec. for the reasons cited above. It seems evident, nevertheless, that commercial pasteurization in this type of machine conforming to a legal minimum specification of 160°F. for a 15-sec. defined holding time will heat-treat the milk considerably beyond the requirement for phosphatase inactivation.

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CREAMING IMPAIRMENT IN HTST PASTEURIZATION OF MILK[1]

By S. A. Hansen,[2] F. W. Wood,[3] and H. R. Thornton[4]

ABSTRACT

The impairment of creaming of milk was studied in a 1000 lb./hr. plate-type HTST pasteurizer, normally equipped with a holding tube with rated "holding time" of 15 sec. Among a number of variables of unknown comparative influence, a first order monomolecular reaction is an important involvement in impairment but the variability in the data is greater than in phosphatase inactivation studies. When the time–temperature requirements for impairment to the end point chosen are plotted on semilogarithmic paper, the observed values follow a straight line having a Z value of 12.4° F. and intersecting the 160° F. abscissa at 15.02 sec. Significant impairment occurs during the heating-up and cooling time intervals. Detectable impairment occurred before phosphatase was inactivated. A cream volume decrease of 1 ml. coincided almost exactly with phosphatase inactivation to the 2 unit/0.5 ml. milk end point. When the legal minimum is 161° F., commercial pasteurization approaches 162° F. for the majority of the milk processed. With a defined minimum holding time of 15 sec. a commercially serious impairment of creaming is probable at this temperature. When cream volume is of critical commercial importance, there appears to be no good justification for setting public health minimum standards higher than 160° F. for 15 sec.

INTRODUCTION

In Sweden a negative phosphatase test is the sole criterion of pasteurization (2). The United Kingdom standard of 162° F. has recently been lowered to 161° F., with 15 sec. as the minimum holding time in each case (10). The United States Public Health Service raised its standard in 1949 (6) to 161° F., where formerly it had been 160° F., and maintained the 15-sec. minimum. The authors are indebted to the Departments of Health of the various Canadian provinces for the information contained in Table I from which it is seen that Canadian standards are not in serious misalignment with those of other countries.

Nevertheless, in a number of Canadian cities complaints are arising that HTST (high-temperature short-time) pasteurization is causing commercially serious impairment of the creaming properties of the milk. There is a growing feeling that the various Canadian regulations governing this process set the minimum standards at unnecessarily high levels. Therefore, since certain aspects of HTST pasteurization were undergoing investigation in this laboratory (7, 8), it was considered important to examine concurrently the creaming impairment effect.

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Contribution from the Department of Dairying, University of Alberta, Edmonton, Alberta.
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This investigation was supported by a grant from the National Research Council of Canada. Issued as Paper No. 291 of the Canadian Committee on Food Preservation.
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[3] *Assistant Professor of Dairying.*
[4] *Professor of Dairying.*

TABLE I

PROVINCIAL REGULATIONS FOR HTST PASTEURIZATION
(as of June 1951)

Province	Minimum standard
Newfoundland	Nil
Prince Edward Island	161° F. – 16 sec.
Nova Scotia	161° F. – 16 sec.
New Brunswick	Nil
Quebec	161° F. – 16 sec.
Ontario	161° F. – 16 sec.
Manitoba	161° F. – 16 sec.
Saskatchewan	160° F. – 15 sec.
Alberta	161° F. – 16 sec.
British Columbia	161° F. – 16 sec.

METHODS

Since the samples for creaming and those for phosphatase assay were taken simultaneously, the pertinent details of the pasteurizer and pasteurization process were as previously particularized (7).

The milk was immediately poured into 100 ml. graduated cylinders carefully selected to include only those with an accuracy of ±0.5 ml. The cylinders, filled in duplicate to the 100 ml. graduation, were stored in ice water for 4 hr. and then at 40° F. for a further 20 hr. Cream layer depth was measured visually at the end of 4 hr. and 24 hr. storage, only the latter of which is reported as it was assumed that the cream volume reached its maximum in this time (11).

The control samples were from the raw milk momentarily heated to 140° F., and then quickly cooled to 45° F. while flowing through a copper coil immersed in ice water. Subsequent treatment was similar to that accorded the HTST pasteurized milks.

Cream volume was read directly from the cylinder graduations and is expressed as milliliters. Thus, 1 ml. cream volume is the equivalent of 1% of the milk volume. Creaming indexes are not reported because, although the fat content of the milk varied within the range 2.8–3.6%, 85% of the milks fell within the range 3.2–3.4%. The creaming indexes, then, became artificial.

The cream volume measurements were sensitive to differences of less than 0.5 ml. Nevertheless, a decrease of 1 ml. (which is probably commercially unimportant (11)) was chosen as the criterion of impairment in order to minimize the element of inaccuracy.

The reader is referred to the many studies of the creaming of milk which have been adequately reviewed elsewhere (4, 5) and need not be repeated here.

RESULTS

Impairment of creaming was measurable in most milks at 155.8° F. when the holding time was normal (15 to 16 sec.) and the control time was 26.5 sec. (Table II). The average cream volume had decreased by 1 ml. at 157.5° F.

When the control time was varied, the cream volume had decreased 1 ml. at the various time–temperature combinations listed in Table III.

As in phosphatase inactivation, control time inadequately expresses the heat-treatment effect, because it ignores the heating-up and cooling intervals. Therefore, Ball's formulas (1) were again applied for evaluating the impairment effects of the heat-treatments beyond the control times and these effects, added to the control times, are included in Table III under the heading "Impairment time".

TABLE II

CREAM VOLUMES IN MILLILITERS AFTER VARIOUS HEAT-TREATMENTS

Milk	Holding time, sec.	Temperature, ° F.										
		Control	155.8	156.8	157.8	158.7	159.7	160.7	161.8	162.9	163.8	164.9
2	15.30	13.75	13.00	13.00	12.25	12.00	11.75	10.75	10.00	9.25	8.50	5.75
3	15.89	12.50	12.00	11.75	11.25	11.00	10.75	10.00	9.25	8.25	7.00	4.75
4	15.41	14.00	13.75	13.00	13.00	12.50	12.00	11.50	10.50	10.00	7.75	6.00
5	15.67	13.00	13.00	13.00	12.75	12.00	11.50	10.75	10.00	8.25	7.00	5.00
6	15.69	12.75	11.50	11.25	11.00	11.00	10.75	10.00	9.25	8.75	8.00	6.25
7	15.85	13.00	13.00	12.50	12.25	12.25	11.50	11.25	10.50	9.50	7.75	6.00
8	15.70	13.00	12.75	12.25	11.75	11.75	11.25	11.00	..	..	..	..
9	15.33	13.00	12.75	12.25	12.25	12.00	11.50	10.75	10.25	9.25	8.50	6.50
10	15.75	13.00	13.00	12.50	11.75	11.75	11.25	10.75	10.00	9.00	7.75	5.25
Average	15.62	13.11	12.75	12.39	12.03	11.80	11.36	10.75	9.97	9.04	7.74	5.69
Average decrease			0.36	0.72	1.08	1.31	1.75	2.36	3.14	4.07	5.37	8.42

TABLE III

TIME–TEMPERATURE REQUIREMENTS FOR CREAMING IMPAIRMENT

Milk	Control time, sec.	Impairment at ° F.	Heating-up equivalent		Cooling equivalent		Impairment time, sec.
			Sec.	%*	Sec.	%*	
11	10.9	159.6	1.8	13.47	0.3	1.94	13.0
12	10.9	160.1	2.2	16.36	0.3	1.83	13.4
13	17.2	159.6	1.8	9.07	0.3	1.31	19.3
14	17.3	158.5	1.2	6.68	0.2	1.28	18.7
15	18.9	158.5	1.2	6.15	0.2	1.18	20.3
16	19.3	159.0	1.4	6.84	0.3	1.17	21.0
17	23.6	157.5	1.0	4.03	0.2	0.91	24.8
18	23.9	157.5	1.0	4.04	0.2	0.90	25.1
19	28.2	155.9	0.8	2.56	0.3	0.86	29.3
20	28.5	155.9	0.8	2.54	0.3	0.85	29.6
21	38.3	155.0	0.6	1.42	0.2	0.60	39.1
22	38.7	155.5	0.5	1.56	0.2	0.57	39.5
23	60.9	152.1	0.5	0.83	0.3	0.41	61.7
24	61.5	151.7	0.5	0.83	0.3	0.43	62.3
25	73.3	151.3	0.5	0.61	0.3	0.38	74.1
26	75.9	151.7	0.5	0.68	0.3	0.35	76.7
27	79.2	151.3	0.5	0.58	0.3	0.35	80.0

* *Expressed as percentage of impairment time.*

Measurable impairment of creaming was evident concurrently with measurable phosphatase inactivation and it is striking that the two reactions were carried to the end points chosen with practically identical heat-treatments (8).

When the average cream volume changes in Table II are plotted on semilogarithmic paper, the values with one exception fall on a straight line (Fig. 1). No explanation is attempted for the exception at 155.8° F.

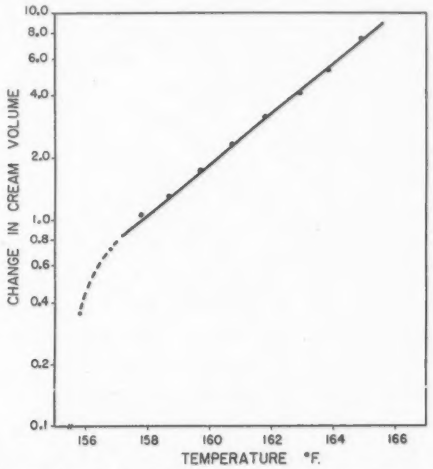

FIG. 1. Cream volume changes in milliliters after heat-treatment at various temperatures with "normal" holding time.

Rate of impairment curves for different milks at various temperatures are, on semilogarithmic paper, straight lines over the major portions of the range of times studied. There were wide variations at either or both ends of the curves. This suggests that impairment is dependent, in part at least, on a first order monomolecular reaction of varying comparative influence in different milks.

When the times required for cream volume impairment of 1 ml. are plotted on semilogarithmic paper against temperature (Table III), the curve of best fit is a straight line having a Z value of 12.4° F., cuts the 160° F. abscissa at 15.02 sec., and is represented by the equation: $T = 174.6 - 12.41 \log t$, where T = temperature in ° F. and t = time in seconds (Fig. 2).

The impairment time 15.02 sec. is the control time plus the heating-up and cooling equivalents. The control times plotted semilogarithmically form a straight line having a Z value of 11.5° F. and intersecting the 160° F. abscissa at 13.34 sec., evidence that creaming impairment during the heating-up and cooling intervals is significant.

Volume time in the present study approaches the time measured in the cell-type apparatus. The volume time equivalent of the 15.02 sec. mentioned above is 21.92 sec. This is within the range 19.8–24.6 sec. found by other investigators (3, 4, 9) at this temperature with cell-type heat-exchangers.

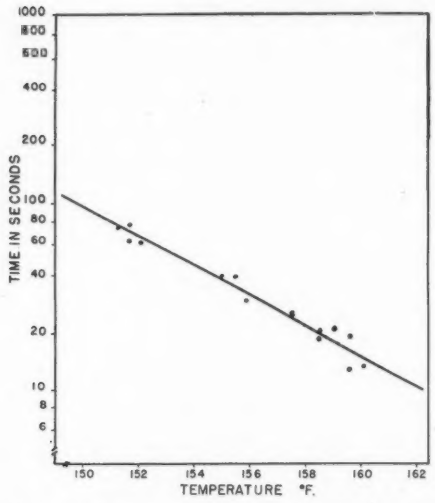

FIG. 2. Time-temperature requirements for creaming impairment.

Accuracy of Results

Cream volume measurements varied over a range of only 0.25 ml. in 12 replicate samples from one milk. On the other hand, the cream volume decrease of 1 ml. was reached in nine milks pasteurized with plate arrangement A and with the normal holding tube at an average temperature of 157.4° F. (range 155.8–158.7° F.), and in seven milks pasteurized with plate arrangement B at an average temperature of 156.33° F. (range 155.9–157.2° F.). Despite this wide variability with different milks, the over-all method when expressed as an average was sufficiently sensitive to detect a small difference in processing technique, since the total effective impairment time was 28.7 sec. with plate arrangement A and 30 sec. with plate arrangement B.

It seems probable that the method of measuring cream volume was sufficiently accurate for a study of this scope and purpose. For the determination of the cream impairment curve, precision meets the disturbing influence of the very variable creaming properties of different milks.

DISCUSSION

The creaming properties of milk depend on a number of variables, some of which are not amenable to modification by the heat of pasteurization. Therefore, a study of the heat-impairment of creaming cannot be expected to yield as uniform results as one involving a single chemical reaction. Cream volume is influenced, among other things, by the clumping factor, which in turn is influenced by the milk euglobulin, a substance susceptible to change by temperature. The inconstancy of the results herein reported is, thus, not surprising and does not warrant the placing of undue credence in their accuracy.

The impairment curve is calculated from a dispersion of points, each of which is representative of only one milk. Individual milks, even of equal fat content, varied widely in their behavior toward the treatment given. Nevertheless, the evidence is strong that a first order monomolecular reaction is an important involvement in heat-impairment of creaming.

In the experimental pasteurizer during normal operation average impairment was just barely less than 2 ml. at 160° F. and was measurably greater than 2 ml. at 161° F. Phosphatase was inactivated and creaming impaired to the end points chosen at almost identical temperatures. Operation beyond that required for phosphatase inactivation quickly led to creaming impairment of commercially serious extent, assuming that point to be reached with a 2 ml. cream volume decrease (11).

To guard against any illegal underpasteurization and, also, against frequent diversion of the milk, it is common practice to set the flow diversion valve for diversion at about 0.5° F. above the legal standard and the heating controls about 0.5° F. above this. Thus, if the legal standard is 160° F., most of the milk will be pasteurized at approximately 161° F., and, if the legal standard is 161° F., most of the milk will be pasteurized at approximately 162° F. At the former temperature cream layer volumes may be reduced 1 ml. in 12.5 sec., assuming instantaneous heating-up and cooling, and at the latter temperature in 10.2 sec. With similar heat-treatment phosphatase is inactivated in 13.3 and 10.4 sec. (8). The time of effective heat-treatment in commercial pasteurizers of the type studied is always considerably greater than the 15-sec. defined holding time, with a consequent and automatic factor of safety of no little magnitude.

The exact relation between phosphatase inactivation and the thermal death time of *Mycobacterium tuberculosis* in the HTST pasteurization region is not known. There is not yet sufficient evidence to justify an assumption that phosphatase is inactivated before *M. tuberculosis* is killed. The weight of available information, indeed, supports the assumption that an adequate factor of safety is attained at 160° F. with the usual defined holding time of 15 sec. When cream volume is a critical consideration in commercial pasteurization, there appears to be no good reason for demanding a higher standard.

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CONTENTS OF VOLUME 31

CORRECTION

Vol. 30, p. 342, 1952. In line 7, "Figs. 2, 3, 4, and 6" should read "Figs. 2, 3, 4, and 5".

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